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OXIDATION OF NITROGEN AND BALL  
LIGHTNING

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Wright-Patterson Air Force Base, Ohio

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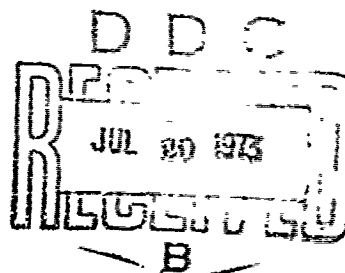
## FOREIGN TECHNOLOGY DIVISION



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by

V. L. Martynov



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## OXIDATION OF NITROGEN AND BALL LIGHTNING

V. L. Martynov

In recent times the interest in ball lightning has grown considerably. It has been the work of the American physicist Barry<sup>1</sup> on experimentally producing a laboratory analog of ball lightning which has stimulated the interest. As Barry describes it, in inducing an electrical discharge in a gas mixture of air and 1.4-1.8% propane there develops a brightly glowing ball of a yellow-green color measuring several centimeters in diameter. The ball "rapidly and haphazardly moves about the chamber and quietly disappears." Its lifetime is about 2 s. When a gas mixture is injected it increases. Under the assumption that the atmosphere contains areas with an increased concentration of hydrocarbon, Barry, at the beginning of his work, describes natural ball lightning as the result of combustion of such hydrocarbons after electrical discharges. The usual concentration of hydrocarbons in the atmosphere does not exceed  $10^{-4}\%$ , and this concentration does not explain all of the examples of the behavior of ball lightning afforded by the model as Barry justly observes at the end of the article. The reason for it again becomes an open question.

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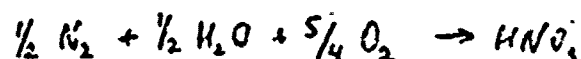
<sup>1</sup>"Journal of Atmospheric and Terrestrial Physics," Vol. 30, 313, 1968.

The thing which most intrigues those who would solve the riddle of ball lightning is the source of its energy. For some the energy enters from the outside (radio waves, electrostatic fields, etc.); for others, and this group predominates, ball lightning is a stable plasmoid which has accumulated the energy of an atmospheric electrical discharge.

If preference is given to the hypothesis of chemical combustion, then we will solve the problem from a different angle. Since the concentration of hydrocarbons in the atmosphere is negligible, we turn to the other components. Let us examine the triple gas system of nitrogen, oxygen, and water vapors - the basic atmospheric ingredient.

Is it possible that in such a system of  $N_2$ ,  $O_2$ , and  $H_2O$  vapors there are chemical processes which occur with heat liberation? It does appear possible - a synthesis of nitric acid based on the oxidation of nitrogen.

The general balance reaction is as follows:



The thermal effect of the reaction<sup>1</sup> for  $H_2O_{liqd}$ ,  $HNO_{3liqd}$ :

$$\Delta H_{298} = -41300 - \left[ \frac{1}{2}(-68320) \right] = -7190 \text{ cal/mole};$$

for the case of  $H_2O$  vapors,  $HNO_3$  vapors:

$$\Delta H_{298} = -3100 \text{ cal/mole.}$$

<sup>1</sup>According to data from the handbooks "Thermodynamic Properties of Individual Substances," Vol. 1,2. Edited by V. P. Glushko, Izd. Academy of Sciences, USSR; M. Kh. Karapet'yants, M. L. Karapet'yants, "Primary Thermodynamic Constants of Inorganic and Organic Substances," 1968.

If we consider possible error in the quantities which are used "for  $H_2O \leq \pm 100$  cal/mole;  $HNO_3 \leq \pm 1500$  cal/mole" the values of the thermal effects will be as follows:

$$\begin{aligned}\Delta H_{298} &= \pm 7190 \pm 1600 \text{ cal/mole} \\ \Delta H_{171} &= -3100 \pm 1600 \text{ cal/mole,}\end{aligned}$$

i.e., and in a refined variation the reaction occurs with heat liberation. The stoichiometric composition of the mixture in volume percentages: nitrogen (22.2%), water vapors (22.2%), oxygen (55.6%), i.e., it differs from earth atmosphere in its concentration of oxygen and water vapors.

Under ordinary conditions such a reaction cannot begin, despite the fact that it occurs with heat liberation - evidence of which is the coexistence of water vapors and air without any type of change. The basic obstacle which prevents the beginning and occurrence of such a reaction is the considerable size of the energy bearer, which is created as energy is expended in "splitting" the nitrogen atom,  $N_2$ .

In the case of a two-component system of  $N_2$  and  $O_2$  the nitric acid is synthesized by means of nitrogen oxides, which, however, unite with the water and produce  $HNO_3$ . On the other hand the formation of the nitrogen oxides is associated with the energy spent (per mole of NO 21,600 cal are spent), and thus the synthesis of  $HNO_3$  is only accomplished by overcoming this energy bearer. Technically this bearer is crossed with an expenditure of the same energy using a somewhat indirect route. First, ammonia is obtained, then it is oxidized into oxides of nitrogen.

Let us examine a three-component system of  $N_2$ ,  $O_2$ , and vapors of  $H_2O$ . In practice is it possible in this system to

make the synthesis reaction of  $\text{HNO}_3$  self-sustaining, taking into account the fact that it occurs with heat liberation? For this reason we must cycle the energy of overall heat liberation to losses involved in the initial "splitting" of the  $\text{N}_2$  molecules. Yet heat liberation begins only after this energy bearer is overcome. We find that there is nothing with which to compensate the initial losses, i.e., the reaction cannot begin spontaneously. In order to "accelerate" it we must artificially introduce energy into the system, so that later, after the losses and heat liberation has been balanced in all stages of the reaction, the system can be brought into a self-sustaining regime. This formation of an energy ring can be achieved by giving the reaction zone the shape of a ball. Note one important condition, which indicates the possibility of constructing and maintaining symmetrical geometry: in volume the original products of the reaction have been  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{H}_2\text{O}$  vapors are 2.25 times greater than the final products - vapors of nitric acid.

Of course, at the present moment it is not possible to fully describe the kinetics of such a process for the three-component system ( $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{H}_2\text{O}$ ). Even for two-component systems, for example, the combustion of carbon monoxide, there is no single viewpoint which covers all the details of the reaction, although the reaction itself has been successfully used for a long time.

For the initial impetus of the reaction we create from the external energy source a high-temperature zone - a "priming region" as it were, with a temperature of  $3500-4500^\circ\text{C}$ . As a result of the temperature effect in this region the water vapors will break down and there will be a dissociation (partial) of the oxygen and nitrogen molecules. These initial expenditures are required in order to overcome the energy bearer, which is linked with the dissociation of the nitrogen molecules. For new portions of the components these expenditures will be compensated by the heat liberated by the reaction which has begun. In the structure



of its thermal fluxes the process is similar to air heating - the incoming components are heated by the outgoing reaction products. The zone in which the reaction occurs acquires the shape of a "burning ball." As mentioned above, conditions do exist for maintaining this shape - in volume the incoming components are 2.25 times greater than the reaction products: thermal pressure will be compensated by the pressure of the radially incoming original components.

As the original moment for describing the interrelated kinetics and structure of the "burning ball" we must study the entire system of  $H_2$ ,  $O_2$ , and  $H_2O$  as a whole, and not just  $H_2$  and  $O_2$  with subsequent addition [to the products of this system of  $H_2O$  vapors. A description of volume reactions for such a]\* triple system at different temperatures cannot be found in the literature. This is not surprising, since volume reactions are extremely complex and branched, even in binary systems. Thus, in the combustion of hydrogen, the most studied system, up to ten different reactions occur, and compounds which are not to be found in the final product appear and disappear:  $O$ ,  $OH$ ,  $KO_2$ ,  $K_2O_2$ ,  $O_3$ .

In a mixture of nitrogen and air oxygen eight different reactions can occur, yielding  $O$ ,  $N$ ,  $O_3$ ,  $NO$ .

It is not difficult to think up a large number of reactions and to arrange their sequence. These might include intermediate compounds such as  $NO$ ,  $HNO$ , and  $OH$ , which are stable at high temperatures. There would be little value in writing them, however. Only a quantitative comparison of experimental data with the retical calculations will enable us to select and describe the necessary sequence of reactions and the branching of chains and will enable us to isolate the active center.

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\*[Translator's Note: Brackets represent later handwritten insertion by the author.]

For the system of  $N_2$ ,  $O_2$  and  $H_2O$  we must describe the reactions in a wide temperature range - from the center of the "burning ball," where the highest temperature is to be found, to the peripheral part with atmospheric temperature.

It might be proposed that the presence of the third component - water vapors - lowers the energy bearer and that the role of the active center belongs not to  $NO$ , but to another compound. Studies of this kind of ternary systems enable us to judge the correctness of opinions which have been expressed.

And now the question: How does ball lightning relate to all of this?

It is proposed that such a self-sustaining combustion of nitrogen occurs in ball lightning. However, the presence of excess nitrogen in relation to the symmetric composition of the reaction leads to the situation where ball lightning exists for a limited time, which at the most can be counted in minutes. The excess nitrogen, which participates in the transport of the incoming components, slows down the reaction. Heat is used to warm it and as a result we have a breakdown in the thermal balance prior to the critical state, where the reaction figures.

A great number of factors must be combined in order to produce ball lightning, and this seldom happens. In addition to optimal air moisture (ball lightning will not develop in dry air), it is important that the induced atmospheric discharge create a high-temperature zone which is of sufficient length, and which exists for the amount of time required to unite the diffusion and transport reaction processes, in other words, the more favorable and longer discharges.

The proposed model represents only a rough approximation of the actual phenomenon. In experimental study it undoubtedly

will reveal a whole range of properties no less interesting. Some of them can be described hypothetically.

1) For the described structure of transport motion of raw and reaction products from the periphery toward the center and vice versa a separation of charges and the formation of electrical layers of different poles, like a spherical condenser, is inevitable because of the disparity in the velocities of the individual ions which participate in the reaction. As the charges accumulate breakdowns develop, which are characterized by crackling and slashes in place of a discharge. It is realistic to assume that the individual charges also have an effect on the chemical processes.

2) Since in volume there is 2.25 times more ingoing components than final products and since the nature of their movement is radial, then there can develop (and in fact is observed) a rotation in ball lightning. The effect has a self-triggering nature and begins when the individual streams of incoming gas deviate from the radial course. In hydrodynamics a close analogy of this effect is the vortex eddys which are formed as a fluid is discharged through an opening which is considerably smaller than the receptacle.

3) The breakdown in the thermal and material balance can either terminate the reaction, resulting in a gradual dispersion of residual heat and components of the system, or the reaction can take the direction of forming new products, in which case the decomposition might have an explosive nature. The possibility of explosive composition does exist, for example,  $\text{NO} + \text{H}_2$ .

The proposed model does not pretend to offer a full explanation for all of the properties and the structure of ball lightning; many statements made are subject to discussion. The most important thing in the opinion of the author is the fact that

an attempt has been made to establish the existence of energy in ball lightning. Any theory which has been experimentally confirmed does have a right to live, and this certainly applies to the present work.